Removal of cadmium from cadmium-contaminated red soils using electrokinetic soil processing[①]

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Abstract: To investigate the feasibility of electrokinetic soil processing on the removal of Cd from Cd-contaminated red soils, a laboratory experiment was conducted. A constant direct current density of $0.5 \, mA/cm^2$ was applied. The result shows that the Cd removal efficiency is remarkably pH-dependent, which is caused by the change of Cd retention capacity of the red soils under different pH conditions. The initial Cd concentration is $1.490 \, g/kg$ and over 79% of it is removed from the red soils after treatment for 96 h. The energy expenditure per unit volume at the end of experiment is about $77.6 \, kW \cdot h/m^3$ and the capital consumed by the whole experiment is $42.6 \, RMB \, Yuan/m^3$, which suggests that the electrokinetic soil processing is a promising technology for remedying Cd-contaminated red soils due to its high removal efficiency and low energy consumption.

Key words: cadmium; electrokinetic soil processing; red soil; electroosmosis

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1 INTRODUCTION

Electrokinetic soil processing(ESP) is one of the newly developed techniques for the remediation of soils. It use low-level direct current of cross-sectional area between the electrodes placed in soils to be treated[1]. Three transport phenomena, electrophoresis, electroosmosis and electromigration, will occur in soils when an electric field is applied to a soil system[2]. Contaminants in fine-grained soils can be transported toward the anode or cathode by means of the electromigration and/or electroosmosis and thus can be removed from soils. Previous studies showed that relatively high removal efficiency of heavy metals could be obtained in fine-grained soils by using ESP[2−5].

pH is a major factor affecting the removal efficiency of heavy metals adsorbed by soils being treated. In order to control the soil pH and enhance the removal efficiency of heavy metals, many methods such as conductive solutions[2, 6], conditioning fluids[7−11], ion selective membrane[8, 12, 13], electrolyte circulation[14], and a porous layer inserted in soils and continuously flushed with conditioning fluids[15], have been used. Since ESP has great potentials in removing heavy metals in fine-grained soils, more and more scientists are now devoting to the studies relating to it. However, in China, only a few people are studying on ESP[3, 5, 10, 11, 16]. Consequently, it is necessary for researchers inland to develop the ESP.

Cd in soils can be classified into soluble and insoluble Cd. The pH value is a major factor affecting the speciation of Cd in soils. Cd in soils may leach into water, especially under acidic conditions. Transformation processes for Cd in soil are affected by the equilibrium of sorption/ desorption and dissolve/ precipitation of Cd. People exposed to low levels of Cd over time may incur kidney damage as well as lung, bone, cardiovascular system, liver and reproductive system damage. Due to its high toxicity, the addition of Cd to soils has the tendency to create environmental pollution and human health problems if it is allowed to enter the food chain. The content of Cd in soils has been increasing continuously in China up to now due to the use of phosphatic fertilizers and additions of sewage sludges, which is threatening to soil quality and human health. Therefore, remediation of soils contaminated by Cd is one of the environmental problems that should be resolved urgently for the moment. The objectives of this paper are to obtain the basic data and to investigate the feasibility of electrokinetic soil processing on the removal of Cd from Cd-contaminated red soils.

2　EXPERIMENTAL

2.1　Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. Inner dimensions of the soil cell are 15 cm × 10 cm × 10 cm. Two sheets of filter paper are placed at each side of the soil cell. Graphite electrodes are used at the anode and the cathode. The pole clearance is approximately 30 cm. 600 mL anolyte and 900 mL catholyte are presented in electrode compartments in order to avoid sudden variations of electrolytes. Meanwhile, the electrolytes are recirculated in electrode compartments by peristaltic pump for the purpose of compensating the loss of electrolytes caused by electrolytic reactions during experiment. The graduated cylinder is used to collecte the electrolytes overflowing from electrode compartments. Therefore, the volume of electroosmotic flow can be obtained from the changes of volume of electrolytes in graduated cylinder.

Four pieces of electrokinetic apparatus were used in this study (Fig. 1). Each of them was removed in turn at a special time for the analysis on the soil pH and the amount of target contaminant remaining in the studied soils.

2.2　Materials

The samples of the red soils were collected from Yuelu Mountain located in Changsha, Hunan Province, China. Some physical and chemical properties of the soil are listed in Table 1. The soils were air dried, and the agglomerates were broken by hand and by using a wooden mallet. Particles larger than 2 mm were removed by sieving. All further tests were performed on the soils with size of less than 2 mm.

About 1 500 mg/L Cd(Ⅱ) solution was prepared by dissolving $Cd(NO_3)_2$ as required in 1 L of deionized water. Each 2 kg sample of air-dried soils was mixed with 1 L prepared solution. The slurry was stirred mechanically for 3 h with an electric stirrer and then settled down for more than 7 d to attain uniform distribution of contaminant and to complete adsorption. After 7 d, four samples with mass of 5 g, two for the determination of initial soil pH and the other for the determination of initial concentration of contaminant, were then taken from the prepared Cd-contaminated soils. Anode purging solution of 0.002 5 mol/L H_2SO_4 and cathode electrolyte solution of 0.25 mol/L H_2SO_4 were used over a 90 h experimental period.

2.3　Methods

Constant current was used to keep the net rates of the electrolysis reactions constant and to minimize the complicated current-boundary conditions. Four pieces of ESP apparatus with the same size are connected in series in the experiment (Fig. 1).

During the experiment, the overall voltage drop between the ends of the soils, the electroconductivity variations of anolyte and catholyte and the volume of electroosmotic flow were measured. Three of the four pieces of ESP apparatus were removed in turn after 24, 48 and 72 h. After removal, soils in each one were sectioned into 5 segments (3 cm in length) for the analysis on the amount of contaminant and soil pH. The soil pH measurement was based on a sample having a soil (dried at 110 ℃)/water ratio of 1∶5. pH meter was used to measure the suspension's pH value. In addition, 50 mL of 0.1 mol/L HCl solution was added into 10 g of soil (dried at 110 ℃) and then the mixture was oscillated in a constant temperature oscillator at 30 ℃ for 1 h (150 r/min). After 1 h, the mixture was filtered. The amount of Cd remaining in each soil segment was obtained by analyzing the filter liquor with AAS after filtration. The parameters in the experiment are summarized in Table 2.
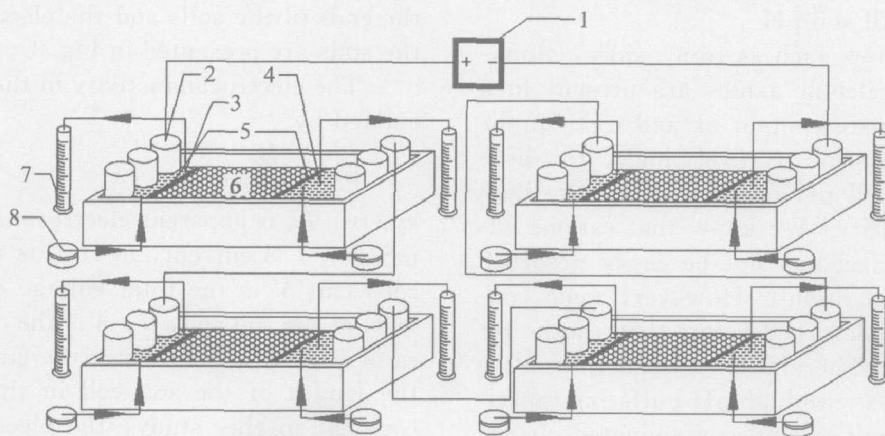

Fig. 1　Schematic diagram of experimental apparatus
1—DC power supply; 2—Graphite electrode; 3—Anolyte; 4—Catholyte;
5—Filter paper; 6—Soil cell; 7—Graduated cyling; 8—Peristaltic pump

Table 1　Chemical and physical properties of red soils

| pH	Permeability coefficient/($m \cdot s^{-1}$)	Content of CEC/ ($mol \cdot kg^{-1}$)	Water content/%	Carbonate content/%	Porosity/ %	Metal background value/($mg \cdot kg^{-1}$)			
						Cd	Pb	Zn	Cu
4.7	6.2×10^{-6}	9.11×10^{-2}	3.01	0.24	45.7	0.16	20	70	22

Table 2　Parameters of ESP in experiment

Initial concentration of contaminant/($g \cdot kg^{-1}$)	Initial soil pH	Cross-sectional area of soil cell/cm^2	Current density/ ($mA \cdot cm^{-2}$)	Duration/ h	Concentration of electrolytes/ ($mol \cdot L^{-1}$)	
					Anolyte	Catholyte
1.49	4.17	100	0.5	96	0.002 5	0.25

3　RESULTS AND DISCUSSION

3.1　Soil pH

Changes of pH values in soil segments bed are shown in Fig. 2. Generally, the soil pH values are less than the initial value of 4.17 after experiment. Under an electric field, hydrogen ions generated at the anode by the electrolysis of water migrate from anode to cathode, resulting in the decrease of the overall soil pH. It is obvious that the pH values in the soil segments near the anode are much lower than those in the vicinity of the cathode. This can be explained by the facts below: firstly, the ionic mobility of hydrogen ions is twice as high as that of the hydroxyl ions generated at the cathode[1]. As a consequence, the length that hydrogen ions transporting through soils is longer than that of hydroxyl ions when they meet. Secondly, in this study, 0.25 mol/L H_2SO_4, which can neutralize the hydroxyl ions generated at the cathode and decrease the amount of hydroxyl ions migrating toward the anode, was used as catholyte. Lastly, as shown in Table 1, the carbonate content and the concentration of CEC of the red soils used in this study are relatively low (0.24% and 9.11×10^{-2} mol/kg, respectively). Therefore, the soils' pH buffering capacity is low, which facilitates the decrease of the overall soil pH.

When impurities such as iron oxides, aluminum oxides and calcium oxides are present in a soil, or the carbonate content or/and CEC of the soils being treated is/are relatively high, it is difficult to make the soil pH decrease due to its high pH buffering capacity. We know that cations adsorbed on soil surface can not be easily desorbed under high pH conditions. However, ionic contaminants must be desorbed before they can be removed from soils. Therefore, soils such as illitic and bentonitic clays with high pH buffering capacity, are more difficult to be decontaminated. In order to lower the soil pH and enhance the removal efficiency of heavy metals in these soils, enhancement techniques such as injecting strong anionic
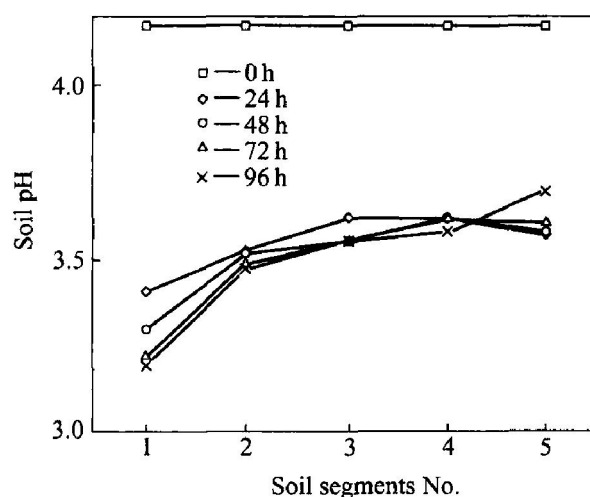
Fig. 2　Changes of soil pH values in soil segments after different times

complexing agents into cathode[17], conditioning technique combined with ion selective membrane[8], and adding an porous layer in soils which was continuously flushed with conditioning fluids, should be applied[15].

3.2　Electric potential difference and electroconductivity in soils

The total electric potential differences between the ends of the soils and the electroconductivity in the soils are presented in Fig. 3.

The electroconductivity in the soils can be calculated by[6]

$$K_a = \frac{IL}{VA} \qquad (1)$$

where　K_a is apparent electroconductivity of soils, mS/cm; I is current, mA; L is the length of soil cell, cm; V is the total voltage drop between the ends of the soil cell, V; A is the cross-sectional area of soil cell, cm^2. Since the current density and the length of the soil cell in the experiment are constant in this study, the electroconductivity is inversely proportional to the voltage drop between the ends of the soils (Fig. 3)
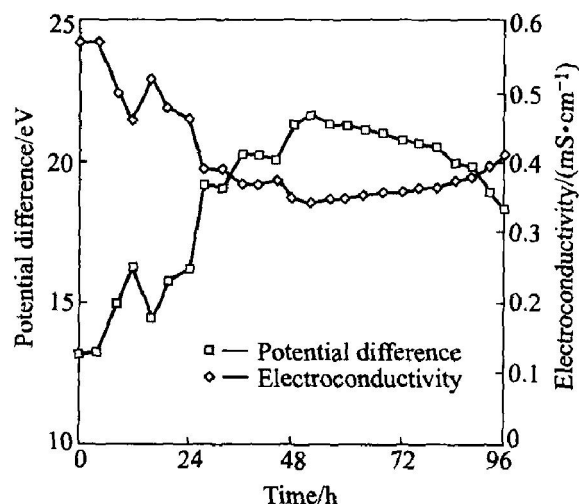
In general, the curve of total electric potential

Fig. 3　Total electric potential difference and electroconductivity at different times

difference vs time shows three regions, the total electric potential difference increasing quickly at the initial stage of experiment, then increasing slowly with time, and decreasing gradually at the last stage of experiment. This phenomenon is remarkably related to the migration of ions in the soils, namely, it is bounded up with the chemical reactions in soils during ESP. Generally, a typical surface functional group, $S(OH)_m$, exists on soil surface and it can accept protons at low pH and dissociate at high pH [18].

$$S(OH)_m + mH^+ \rightleftharpoons S(OH_2)_m^{m+} \qquad (2)$$
$$S(OH)_m \rightleftharpoons S(O_m)^{m-} + mH^+ \qquad (3)$$
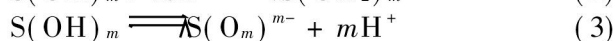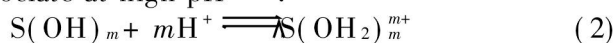
where $S(OH_2)_m^{m+}$ is the protonized $S(OH)_m$, $(SO_m)^{m-}$ is the product of $S(OH)_m$ after its dissociation. Metal ions in soils can hydrolyze and form hydroxyl complexes. These hydroxyl complexes can be adsorbed by soils. The adsorption reaction is given by

$$S(O_m)^{m-} + M_L^{n+} \rightleftharpoons (SO_m - M_L)^{(m-n)-} \qquad (4)$$

where M_L^{n+} is the metal ions existing as the dissociated state, $(SO_m - M_L)^{(m-n)-}$ is the metal ions adsorbed by soils. Combining Eqns. (3) with (4) yields

$$S(OH)_m + M_L^{n+} \rightleftharpoons (SO_m - M_L)^{(m-n)-} + mH^+ \qquad (5)$$

At the initial stage of experiment, some hydrogen ions generated at anode are adsorbed by the red soils during its migration toward the cathode (Eqn. (2)), resulting in the decrease of the amount of ionic conductor. For this reason, the voltage drop in soils increases and the electroconductivity of soils decreases. As time passes, the concentration of hydrogen ions increases gradually caused by electrolysis of water, resulting in the equilibrium in Eqn. (5) moving toward left. Therefore, the Cd(II) adsorbed by the red soils is gradually desorbed from soil surface and thus the

amount of ionic conductor in soils increases constantly, resulting in the decrease of the total electric potential difference and the increase of the electroconductivity in the soils.

The distributions of electric potential differences in the soils are shown in Fig. 4. At first, potential gradients have no big changes. However, the electric potential change fast and become space related after many hours.
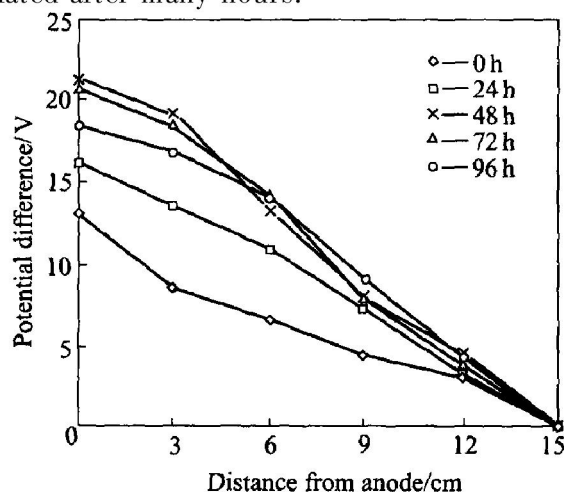

Fig. 4　Electric potential difference across soils after different times

The biggest one among the five potential gradients is in the region from 6 cm to 9 cm, increasing from initial value of 0. 7 V/ cm to 2. 03 V/ cm after 72 h treatment. Although it subsequently decreases to 1. 7 V/ cm, it remains the biggest one. The potential gradients in the vicinity of the cathode are the second and those in the regions near the anode are the third. The reasons for this phenomenon may be: 1) The transportation of hydrogen ions from anode to cathode results in that the concentration of hydrogen ions in the regions near the anode is higher than that in the regions close to the cathode. Consequently, the potential gradients in the latter are bigger than those in the former. 2) 0. 25 mol/ L H_2SO_4 which has relatively high concentration of hydrogen ions, was used as catholyte. Notwithstanding that it can be neutralized by hydroxyl ions produced at the cathode, hydrogen ions concentration difference between catholyte and soil pore water exists yet. As a result, hydrogen ions diffuse freely from cathode to anode due to its high diffusion coefficient, resulting in that the amount of ionic conductor in the vicinity of the cathode is bigger than that in the midmost region. Therefore, the potential gradient in the midmost region of soils is the biggest one.

3. 3　Electroconductivity in electrolytes and electro-osmotic flow

Variations of the electroconductivity in elec-

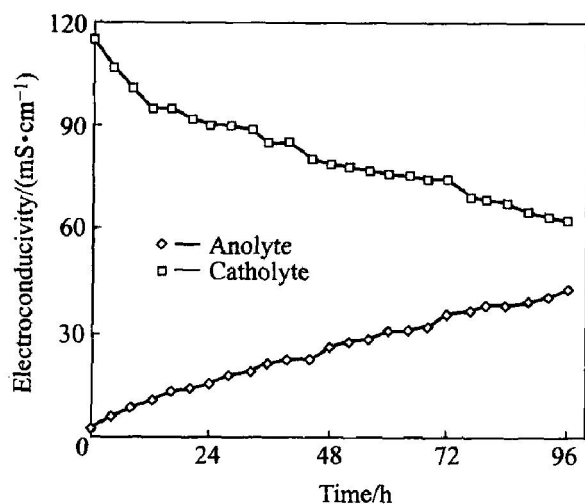trolytes are shown in Fig. 5.

Fig. 5 Electroconductivies of anolyte and
catholyte at different times

As hydrogen ions were produced by the electrolysis of water, electroconductivity in anolyte increases slowly from 2. 20 to 42. 6 mS/ cm. However, the catholyte (sulfuric acid) were buffered by hydroxyl ions produced in the cathode, which result in that the electroconductivity in catholyte decreases gradually from 115 to 62. 8 mS/ cm.

The change of cumulative electroosmotic flow volume with time is shown in Fig. 6. The cumulative electroosmosis flow volume transported toward the cathod increases with time in the initial stage of experiment.
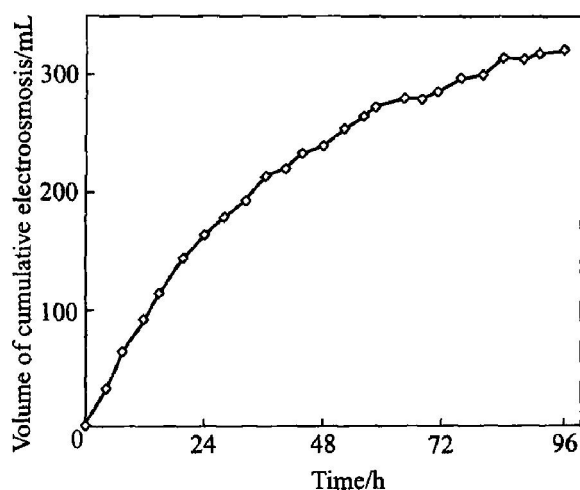

Fig. 6 Volume change of electroosmotic flow
with time

The main factors affecting the electroosmotic flow in the soil system are soil pH, applied electric field intensity and soil permeability. Since the pH and electroconductivity of the anolyte control the soil pH and the electroconductivity in soils, the anolyte may affect electroosmosis in soils. Electro-

osmotic velocity on a plane surface (v_{eo}), is expressed as[19]

$$v_{eo} = \frac{\varepsilon \zeta E_x}{\mu} \qquad (6)$$

where ε is permittivity of the pore liquid, C/ (V • m); ζ is zeta potential of the soil, V; E_x is electric field (V/ m) parallel to direction of electroosmotic flow, and μ is viscosity of the pore liquid (N • s/ m^2). According to the Eqn. (6), the electroosmotic velocity is significantly affected by the zeta potential. Generally, the zeta potential of most soils is negative because of a negative charge carried by soil surfaces. Therefore, electroosmotic flow is generally toward the cathode. However, when the cationic concentrations in soil pore water increase caused by increase of the cationic concentrations in the anolyte, the cations adsorbed on the surface of the clay particles will increase. The increased cations will result in decrease of the zeta potential and the electroosmotic velocity. Consequently, the decrease of the soil pH and the increase of the electroconductivity of soil pore water will make the electroosmotic velocity decrease. Based on above-mentioned descriptions, the increment of the volume of electroosmotic flow decreases significantly from the middle stage of the experiment (Fig. 6). Furthermore, when the zeta potential becomes positive, the electroosmotic flow will reverse, which was observed in a few experiments[15, 17]. The reversal of electroosmosis is helpless to the removal of heavy metals in contaminated soil because it is contrary to the direction of movement of metallic cations. Negative zeta helps the electroosomosis transport toward the cathode. Low pH accelerates the dissolution and desorption of metal contaminants but facilitates the increase of the zeta potential. Therefore, how to simultaneously maintain the negative zeta potential and low pH in soils is the key in the successful implementation of the ESP.

3. 4 Cd Concentration in soils and energy consumption

The distributions of Cd at different experimental stgaes are shown in Fig. 7.

Under the electric field, that the hydrogen ions move from the anode toward the cathode makes the Cd desorb from the red soil surface. The desorbed Cd then gradually migrates toward the cathode by electromigration and electroosmosis, resulting in the decrease of the overall amount of Cd in the soils. The actions of hydrogen ions are diplex. On the one hand, the increase of hydrogen ions in the anolyte makes the hygrogen ions in the double layer increase. On the other hand the inner sphere complexes occuring at the interface between the soil particles and soil pore water make the val-
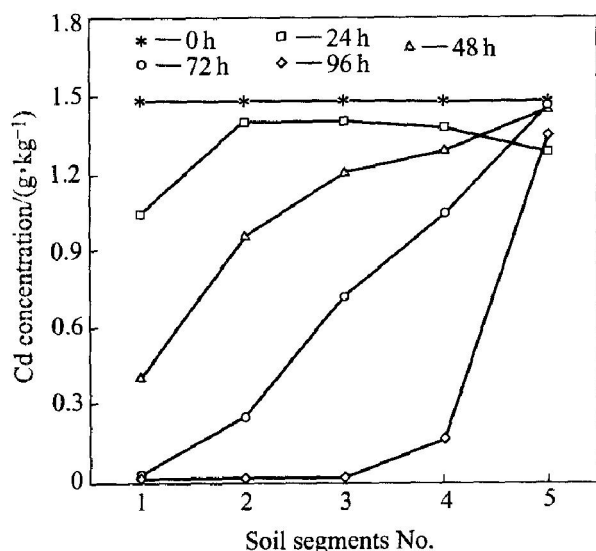
Fig. 7   Cd concentrations in red soil segments

ue of the negative surface charge decrease, which is helpless to ESP because it makes the electroosmosis transport toward the cathode decrease.

Fig. 8 shows the relationship between soil pH and Cd-removal efficiency. After experiment, the final soil pH and Cd-removal efficiency in segment 1 are 3.18% and 99.42%, respectively while those in segment 5 are 3.69% and 9.4%, respectively. It is obvious that the Cd-removal efficiency is pH-dependent. This pH-dependence may be explained by the change of Cd retention capacity of the red soils with the change of soil pH [20].
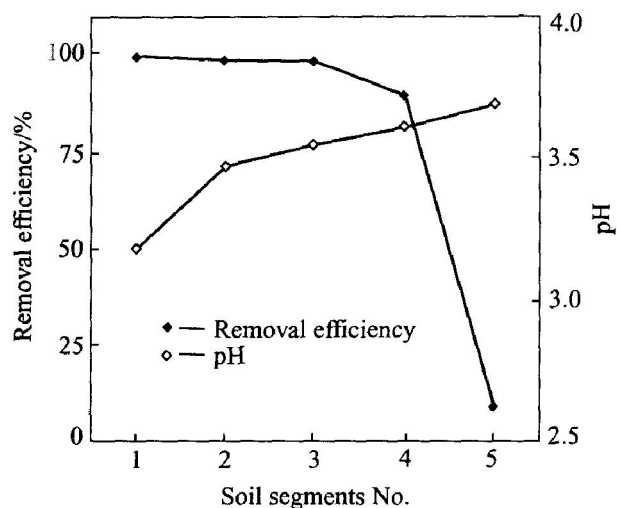

Fig. 8   Relationship between soil pH and
Cd-removal efficiency

After treatment for 96 h, 79.18% of Cd is removed from the red soils. The removal efficiency of Cd, presumably, will be much higher if we prolong the experimental period. With a constant current density of 0.5 mA/cm^2 and a treatment period of 96 h, the calculated energy consumption is 1.164×10^{-1} kW • h. Since the volume of the soil

cell is 1 500 cm^3, the energy expenditure per unit volume at the end of experiment is about 77.6 kW • h/m^3. According to the standard electricity price of 0.549 RMB Yuan/(kW • h) for ordinary industry in Changsha, China, the capital consumed by the whole experiment is 42.6 RMB Yuan/m^3, which indicates that ESP, due to its high removal efficiency and low energy consumption, is a promising remedial technique for the removal of Cd in red soils.

4   CONCLUSIONS

ESP is a promising technique for remedying Cd-contaminated red soils due to its high Cd-removal efficiency and low energy consumption. pH and electroosmosis are the major factors affecting the Cd removal efficiency. Low soil pH accelerates the desorption of adsorbed Cd and thus it helps to remedy the contaminated soils. At the same time, low soil pH will also make the electroosmosis transported toward the cathode decrease, which is helpless to the electrokinetic remediation. Therefore, the key of the successful implementation of ESP is how to control the soil pH so as to make the soils being treated in low pH conditions, while the electroosmosis will not reverse its direction.

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